

United States Environmental Protection Agency Washington, DC 20460				Work Assignment Number: <b>1-23</b> <input checked="" type="radio"/> Original Amendment				
<b>Work Assignment</b>								
Contract Number: EP-C-09-027		Contract Period Base: 04/01/2010 - 03/31/2011 Option Period No. 1		SF Site Name:				
Title of Work Assignment: Combustion Fine PM								
Suggested Source: Arcadis			Specify Section & Paragraph of Contract SOW: B.2, H.19, H.20, H.23, H.30, H.31, H.32, I.5,					
Purpose: <input checked="" type="radio"/> Work Assignment Initiation <input type="radio"/> Work Assignment Close-Out <input type="radio"/> Work Assignment Amendment <input type="radio"/> Incremental Funding <input type="radio"/> Work Plan Approval			Period of Performance From: 05/10/2010 To: 03/31/2010					
Comments: Initiate WA to continue LOE previously covered by WA 0-23. See attached SOW.			WAC Category (check one) <input type="radio"/> I Enforcement <input type="radio"/> II Standard Setting <input type="radio"/> III Technology Development <input checked="" type="radio"/> IV Proof of Concept <input type="radio"/> N/A					
Note: To report additional accounting and appropriations data use EPA Form 1900-69A.								
SFO 22 Superfund (Max 2)		Accounting and Appropriations Data						
		Non-Superfund						
DCN (Max 6)	Budget/FYs (Max 4)	Appropriation Code (Max 6)	Budget Org/Code (Max 7)	Program Element (Max 9)	Object Class (Max 4)	Amount	Sites/Project (Max 8)	Cost Org/Code (Max 7)
1								
2								
3								
4								
5								
<b>Authorized Work Assignment Ceiling</b>								
Contract Period:			Cost/Fee			LOE		
Previously Approved			New			0		
This Action						0		
Total						0		
<b>Work Plan / Cost Estimate Approvals</b>								
Contractor WP Dated:			Cost/Fee:			LOE:		
Cumulative Approved:			Cost/Fee:			LOE:		
Work Assignment Manager Name: Bill Linak (Signature) (Date) 5/10/10			Branch / Mail Code: APTB / E305-01 Phone Number: (919) 541-5792 Fax Number: 919-541-0554					
Branch Chief Name: Robert E. Hall, Chief, APTB (Signature) (Date) 5/5/10			Branch/Mail Code: APTB / E305-01 Phone Number: (919) 541-2477 Fax Number: 919-541-0554					
Project Officer Name: Diane Pierce (Signature) (Date) 5/7/10			Branch/Mail Code: TSB / E343-03 Phone Number: (919) 541-2708 Fax Number: 919-541-0496					
Contracting Official Name: Renita Tyus, CO (Signature) (Date) 5/10/10			Branch/Mail Code: CPOD Phone Number: (513) 487-2094 Fax Number: (513) 487-2109					
Contractor Acknowledgement of Receipt and Approval of Workplan (Signature and Title)						Date		

## Scope of Work **Combustion Fine PM**

This WA contains three tasks to generate, collect, and characterize particulate matter (PM) and other pollutants from stationary combustion sources burning fossil fuels (coals, fuel oils, gasoline, petro-diesel) and biofuels (wood, glycerol, ethanol, bio-diesel). Portions are being conducted in collaboration with NHEERL investigators to perform exposures and collect PM for health studies. Task 1 describes collection and characterization methods. Tasks 2 and 3 describe modification, operation, support, and maintenance of three experimental facilities used to generate these samples.

The contractor shall perform the following tasks:

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### **Task 1. Combustion Particles – Collection, Physical and Chemical Characterization**

#### **Background**

Combustion particles are ubiquitous ambient air contaminants derived from a large variety of mobile and stationary sources. Exposure to combustion PM is associated with carcinogenic and immunotoxic effects in humans and experimental animals. At the cellular level, these health effects are underlain by genotoxic and inflammatory properties of chemical compounds present in the PM. Combustion PM is composed of elemental, inorganic and organic compounds that vary widely in composition with the source of the fuel, combustor/boiler/engine operating conditions, sampling methods and other parameters. The genotoxic and inflammatory potencies of combustion PM also vary with its physicochemical properties, and these differences along with multiple health effects impede the development of targeted regulatory strategies for mitigating the impact of combustion PM exposure on human health. Combustion emissions shall be generated, and PM samples shall be collected using a number of fuels, fuel additives, combustor/boiler/engine types, operating conditions, and collection techniques. These PM samples shall then be stored and characterized through extensive chemical and physical analyses. In conjunction with the chemical and physical analyses (described above), whole particles and extracts shall be provided to NHEERL investigators for subsequent determination of inflammatory and genotoxic potencies.

#### **Objectives / Scope of Work**

The objectives of this WA task are to generate and collect a number of combustion PM samples with different physical, chemical, and toxicological properties, and (in conjunction with NHEERL investigators) and correlate differences in the PM properties with adverse health effects and mechanisms of toxicity.

Combustion PM samples shall be analyzed for size and morphology during production while detailed chemical analysis shall be performed post-collection. Physical measurements shall include particle size distributions using a scanning mobility particle sizer (SMPS) and an aerodynamic particle sizer (APS). Particle concentrations shall be assessed with gravimetric filters and TEOM instrumentation. Particle morphology shall be examined by scanning and transmission electron microscopy. Chemical analysis shall involve qualitative analysis by aerosol time of flight mass spectroscopy (ATOF-MS), quantification of elemental and organic carbon (OC/EC), inorganic trace element analysis by x-ray fluorescence (XRF) and inductively coupled plasma-mass spectroscopy (ICPS). Additional samples shall be subjected to solvent extraction with dichloromethane (DCM), and then sequential fractionation using hexane, 50% hexane/50% DCM, DCM, and methanol to determine the relative concentrations of polar and non-polar compounds. Extract mass shall be determined gravimetrically. Organic extracts shall be further analyzed using gas chromatography in conjunction with mass spectroscopy (GC-MS) in the full scan mode. Acquired spectra shall be searched against a computerized mass spectral library and shall also be reviewed manually. Standards of both PAHs and nitro-PAHs shall be analyzed and semi-quantitative values shall be obtained by comparing area ratios of any particular peak to the internal standard. Approximately 25 peaks shall be

examined and emphasis shall be placed on those peaks that appear to differ between the samples. Since many of the more polar compounds may not be detected by the GC-MS because of their volatility, high performance liquid chromatography in conjunction with Ion Trap Mass Spectroscopy (LC-MS) shall be performed. In addition to organic analysis, PM samples may be characterized by electron paramagnetic resonance (EPR) analysis for presence and concentration of stable free radical species.

#### Deliverables

The contractor shall deliver raw analytical data (computer files and data sheets) and reduced data in the form of Excel spreadsheets, pie charts, and graphs of the data collected for each PM sample.

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### **Task 2. Metal Fuel Additives for Soot Reduction – Diesel Engines and Atmospheric Pressure Diffusion Flames**

#### Background

Metal-based catalysts are added to diesel fuels with the intention of increasing fuel economy and reducing emissions. These fuel borne catalysts (FBCs) are divided into a class of liquid-phase organo-metallic materials that form nano-scale particles during the combustion process, and a class of solid-phase nano-scale metal oxides that are added to fuel and kept in suspension with surfactants. Commercially available formulations include (but are not limited to) compounds containing iron (Fe), platinum (Pt), and cerium (Ce).

While studies have shown that metal FBC additives can reduce particle mass emissions, there is also evidence that they may increase particle number emissions and otherwise affect the physical and chemical characteristics of diesel exhaust emissions and may result in increased levels of some air toxic chemicals such as benzene, 1,3-butadiene, acetaldehyde. Unless the use of metal FBCs is done in conjunction with diesel particulate filters (DPFs) their use will likely increase the ambient emissions of these metals. Research questions include to what extent do metal FBCs affect diesel related particulate and air toxics emissions (especially in the ultrafine size range <100 nm), and the potential health effects associated with the large-scale application of metal FBCs.

#### Objectives / Scope of Work

The objectives of this WA task are to operate and maintain two existing experimental facilities designed to examine emissions from combustion with metal FBC additives. These include a Burke-Shumann diffusion flame experiment designed to examine metal FBCs applied to sooting gaseous fuels (ethylene) and a small diesel engine gen-set with controlled dilution designed to examine metal FBCs in engines. Improvement to the existing facilities and development of new experimental capabilities are anticipated. The objectives of this research are to design and execute parametric studies to characterize the physical and chemical properties of gas and particle emissions with and without metal FBCs (Fe, Pt, and Ce). This study may also take advantage of the existing animal exposure facility, and collaboration with NHEERL investigators to perform animal exposure experiments, and collect appropriate samples for instillation studies.

Combustion PM samples shall be analyzed using techniques similar to those identified in Task 1.

#### Deliverables

The contractor shall deliver raw analytical data (computer files and data sheets) and reduced data in the form of Excel spreadsheets, pie charts, and graphs of the data collected for each parametric study.

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### **Task 3. Glycerol Combustion**

## Background

Glycerol, glycerine, or Propane-1,2,3-triol is a compound used as a component in medical and pharmaceutical products, livestock feeds, lubricants, food additives, plastics, nitroglycerine, antifreeze, and fabrics. Glycerol is currently produced during saponification of fats (soap making) and transesterification of triglycerides (biodiesel production). While pure glycerol is a marketable commodity, the recent growth of the biodiesel industry has flooded the market with an excess supply of glycerol. This has caused a substantial continual drop in the price of glycerol.

Biodiesel is produced from the transesterification of triglycerides (most commonly from vegetable oils or animal fats) via reaction with an alcohol (typically methanol) and a catalyst to produce fatty acid methyl esters (FAME, the biodiesel molecules), and glycerol. The common base catalysts are potassium hydroxide and sodium hydroxide. Volumetrically, for every 10 units of biodiesel produced, roughly one unit of glycerol byproduct is created and must be disposed. In a large-scale biodiesel facility, this can amount to millions of gallons of crude glycerol a year. Some biodiesel operations have successfully used crude glycerol as livestock feed additives and fertilizers. Still many currently pay to have glycerol shipped away to landfills. Thus, it is important to find new value added uses (including applications as fuels) for waste glycerol. Glycerol combustion could also be a key factor in the development of new second generation biodiesel processes, which require large thermal inputs and also creates waste glycerol. Heating the reactants can significantly increase the transesterification reaction rate, and so any large biodiesel plant will typically need to use a significant amount of thermal energy. Burning glycerol for process heating would offset energy costs, eliminate transportation costs (plants could burn their own glycerol on site), and act as an effective mode of disposal. However, the difficulty of burning glycerol has prevented this from becoming a chosen solution in the biodiesel industry.

Glycerol is much more difficult to burn than conventional hydrocarbon fuels. While glycerol contains significant energy, its energy density is much less than fuel oils. One kilogram of glycerol contains roughly 16 MJ of chemical energy, in comparison to kerosene, which has 42.8 MJ/kg, or gasoline with 44.4 MJ/kg. Glycerol is also a highly viscous liquid at room temperature, with a kinematic viscosity over 450 centistokes, compared with water which has a kinematic viscosity of 1 cS. Kerosene has a kinematic viscosity of 2.71 cS, and gasoline falls between 0.46 to 0.88 cS, depending on the grade. The high viscosity of glycerol makes it impossible to atomize cold pure glycerol using standard nozzles found in fuel oil burners. It should be noted that waste glycerol from biodiesel production may contain some alcohol which will lower the viscosity, but many biodiesel producers prefer to evaporate and recover the alcohol from the glycerol for reuse. Glycerol can also be heated to dramatically reduce its viscosity, with a viscosity approaching that of #2 fuel oil at 100 C. Initial small-scale experiments at NCSU have demonstrated the efficient burning of glycerol in a high-swirl burner with propane preheating and air-blast nozzles.

## Objectives / Scope of Work

The objectives of this WA task are to examine issues associated with glycerol combustion in larger more realistic combustion hardware. Initial efforts will use the Rainbow furnace (200 kBTU/hr) and move to the North American boiler (2 MBTU/hr). Glycerol atomization using pressure and dual-fluid nozzles shall be investigated. Flame stability and emissions shall be examined co-firing glycerol with varying amounts of natural gas and/or No. 2 fuel oil. Emissions measurements shall include available continuous emission monitors (O<sub>2</sub>, CO, CO<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub>, THC), particulate mass (filter and TEOM), particle size distribution (SMPS/APS), and inorganic and organic compositions. Volatile aldehydes and other oxygenated HAPs are of particular concern due to the highly oxygenated composition of the fuel. This project is in collaboration with Dr. Bill Roberts (NCSU), who will provide the waste glycerol.

## Deliverables

The contractor shall deliver raw analytical data (computer files and data sheets) and reduced data in the form of Excel spreadsheets, pie charts, and graphs of the data collected for each experimental study.

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#### General Support

The contractor shall provide technical support, operating experience, analytical support, and expendable materials to conduct these tests using existing in-house combustion systems or through the fabrication, rental, purchase, or lending of additional combustion equipment as necessary. This support shall include:

1. The contractor shall provide expendable materials and building supplies to modify, operate, and maintain the necessary combustion equipment, as appropriate.
2. The contractor shall provide engineering and operating labor for the design and execution of test plans on these furnaces and engines.
3. The contractor shall maintain, calibrate, and operate monitoring equipment according to APPCD's Recommend Operating Procedures (ROPs), QAPP requirements, safety requirements, and instrument manuals.
4. The contractor shall collect and retain necessary operational data to ensure compliance with NC Air permit reporting requirements.
5. The contractor shall operate and maintain the experimental systems and air pollution control system in full compliance of NC Air permits.

#### Quality Assurance Project Plans (QAPPs)

The contractor shall perform the activities described in Tasks 1-3 in accordance with the QAPPs entitled:  
DEP Collection - QTRAK 04033 9/4/07

Combustion Particle Analysis - QTRAK 07048 1/15/09

Generation and Delivery of DEP for Health Effects - QTRAK 98018 8/7/07

PM Emissions from a Drop Tube Furnace - QTRAK 02062 1/1/05

Glycerol Combustion – QTRAK 09053 10/5/09

The contractor shall revise or amend these QAPPs as needed in accordance with quality assurance requirements. If revisions are necessary, data acquisition shall not commence until official approval is received from EPA Quality Assurance Staff. The contractor shall comply with all requirements as delineated on the "Quality Assurance Review Form" included with this extramural action.

#### Documentation of Technical Direction

The WAM and contractor's project manager shall schedule weekly project meeting in which task progress, issues, and future direction shall be discussed. The contractor's project manager shall summarize the notes from each of these meetings in the form of an e-mail message to the WAM. This summary shall help assure clear communication, establish project priorities, and provide documentation of technical direction.

#### Reports of Work

The following reports of work shall be provided.

1. Monthly progress reports with labor costs and ODC charges.

2. Health and safety plans as required by EPA safety officer.
3. The contractor shall comply with all requirements as delineated on the "Quality Assurance Planning Requirements Form" included with this extramural action.
4. Update Facility Manuals as required by EPA QA officer.
5. Operate Compliance reports as required by NC Air permits.

## **ATTACHMENT #1 TO THE STATEMENT OF WORK (SOW) FOR MEASUREMENT PROJECTS**

### **NRMRL Quality Assurance (QA) Requirements**

In accordance with EPA Order 5360.1 A2, conformance to ANSI/ASQC E4 must be demonstrated by submitting the quality documentation specified herein. All quality documentation shall be submitted to the Government for review. The Government will review and return the quality documentation, with comments, and indicate approval or disapproval. If the quality documentation is not approved, it must be revised to address all comments and shall be resubmitted to the Government for approval. Work involving environmental data collection, generation, use, or reporting shall not commence until the Government has approved the quality documentation. The quality documentation shall be submitted to the Government at least thirty (30) days prior to the beginning of any environmental data gathering or generation activity in order to allow sufficient time for review and revisions to be completed. After the Government has approved the quality documentation, the Contractor shall also implement it as written and approved by the Government. Any EPA-funded project/program may be subject to a QA audit.

#### **TO BE SUBMITTED PRE-AWARD (mark all that apply):**

☐ **NRMRL's Quality System Specifications:**

- (1) a description of the organization's Quality System (QS) and information regarding how this QS is documented, communicated and implemented;
- (2) an organizational chart showing the position of the QA function;
- (3) delineation of the authority and responsibilities of the QA function;
- (4) the background and experience of the QA personnel who will be assigned to the project; and
- (5) the organization's general approach for accomplishing the QA specifications in the SOW.

- ☐ **Quality Management Plan:** prepared in accordance with R-2 - EPA Requirements for Quality Management Plans (EPA/240/B-01/002) March, 2001,  
<http://www.epa.gov/quality/qs-docs/r2-final.pdf>

#### **TO BE SUBMITTED POST-AWARD (mark all that apply):**

☐ **NRMRL's Quality System Specifications:**

- (1) a description of the organization's Quality System (QS) and information regarding how this QS is documented, communicated and implemented;
- (2) an organizational chart showing the position of the QA function; 07/14/08 A-2
- (3) delineation of the authority and responsibilities of the QA function;
- (4) the background and experience of the QA personnel who will be assigned to the project; and
- (5) the organization's general approach for accomplishing the QA specifications in the SOW.

- ☐ **Quality Management Plan:** prepared in accordance with R-2 - EPA Requirements for Quality Management Plans (EPA/240/B-01/002) March, 2001,  
<http://www.epa.gov/quality/qs-docs/r2-final.pdf>

- ☐ **Category I or II Quality Assurance Project Plan (QAPP):** prepared in accordance with R-5 - EPA Requirements for QA Project Plans (EPA/240/B-01/003) March, 2001  
<http://www.epa.gov/quality/qs-docs/r5-final.pdf>

- ☒ **Category III or IV QAPP:** prepared in accordance with applicable sections of the following NRMRL QAPP Requirements List(s) which is(are) included in this attachment:

## **X QAPP Requirements for Measurement Projects**

- ☐ **QAPP Requirements for Secondary Data Projects**
- ☐ **QAPP Requirements for Research Model Development and/or Application Projects**
- ☐ **QAPP Requirements for Software Development Projects**
- ☐ **QAPP Requirements for Method Development Projects**
- ☐ **QAPP Requirements for Design, Construction, and/or Operation of Environmental Technology Projects**

### **ADDITIONAL QA RESOURCES:**

EPA's Quality System Website: <http://www.epa.gov/quality/>

EPA's Requirements and Guidance Documents: [http://www.epa.gov/quality/qa\\_docs.html](http://www.epa.gov/quality/qa_docs.html)

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## **NRMRL QAPP REQUIREMENTS FOR MEASUREMENT PROJECTS**

### **GENERAL REQUIREMENTS:**

Include cover page, distribution list, approvals, and page numbers.

#### **0. COVER PAGE**

Include the Division/Branch, project title, revision number, EPA technical lead, QA category, organization responsible for QAPP preparation, and date.

#### **1. PROJECT DESCRIPTION AND OBJECTIVES**

- 1.1 Describe the process and/or environmental system to be evaluated.
- 1.2 State the purpose of the project and list specific project objective(s).

#### **2. ORGANIZATION AND RESPONSIBILITIES**

- 2.1 Identify all project personnel, including QA, and related responsibilities for each participating organization, as well as their relationship to other project participants.
- 2.2 Include a project schedule that includes key milestones.

#### **3. SCIENTIFIC APPROACH**

- 3.1 Describe the sampling and/or experimental design that will be used to generate the data needed to evaluate the projective objective(s). A description of the design should include the types and numbers of samples (including QC and reserve samples), the design of the sampling network, sample locations and frequencies, and the rationale for the design.
- 3.2 Identify the process measurements (e.g., flow rate, temperature) and specific target analyte(s) for each sample type.
- 3.3 Describe the general approach and the test conditions for each experimental phase.

#### **4. SAMPLING PROCEDURES**



- 4.1 Describe any known site-specific factors that may affect sampling procedures as well as all site preparation (e.g., sampling device installation, sampling port modifications, achievement of steady-state) needed prior to sampling.
- 4.2 Describe or reference each sampling procedure (including a list of equipment needed and the calibration of this equipment as appropriate) to be used. Include procedures for homogenizing, compositing, or splitting of samples, as applicable.
- 4.3 Provide a list of sample containers, sample quantities to be collected, and the sample amount required for each analysis, including QC sample analysis.
- 4.4 Specify sample preservation requirements (e.g., refrigeration, acidification, etc.) and holding times.
- 4.5 Describe the method for uniquely numbering each sample.
- 4.6 Describe procedures for packing and shipping samples, including procedures to avoid cross-contamination, and provisions for maintaining chain-of-custody (e.g., custody seals and records), as applicable.

## **5 MEASUREMENT PROCEDURES**

- 5.1 Describe in detail or reference each process measurement or analytical method to be used. If applicable, identify modifications to EPA-approved or similarly validated methods.
- 5.2 If not provided in Section 5.1 or the referenced method, include specific calibration procedures, including linearity checks and initial and continuing calibration checks.

## **6 QUALITY METRICS (QA/QC CHECKS)**

- 6.1 For each process measurement and analytical method, identify the required QC checks (e.g., blanks, control samples, duplicates, matrix spikes, surrogates), the frequencies for performing these checks, associated acceptance criteria, and corrective actions to be performed if acceptance criteria are not met.
- 6.2 Any additional project-specific QA objectives (e.g., completeness, mass balance) shall be presented, including acceptance criteria.

## **7 DATA ANALYSIS, INTERPRETATION, AND MANAGEMENT**

- 7.1 Identify the data reporting requirements, including data reduction procedures specific to the project and applicable calculations and equations.
- 7.2 Describe data validation procedures used to ensure the reporting of accurate project data.
- 7.3 Describe how the data will be summarized or analyzed (e.g., qualitative analysis, descriptive or inferential statistics) to meet the project objective(s).
  - 7.3.1- If descriptive statistics are proposed, state what tables, plots, and/or statistics (e.g., mean, median, standard error, minimum and maximum values) will be used to summarize the data.
  - 7.3.2- If an inferential method is proposed, indicate whether the method will be a hypothesis test, confidence interval, or confidence limit and describe how the method will be performed.
- 7.4 Describe data storage requirements for both hard copy and electronic data.

## **8 REPORTING**

- 8.1 List and describe the deliverables expected from each project participant responsible for field and/or analytical activities.
- 8.2 Specify the expected final product(s) that will be prepared for the project (e.g., journal article, final report).

## **9. REFERENCES**

Provide references either in the body of the text as footnotes or in a separate section.